

EVOLUTION OF CO₂ AND H₂O ON MARS: A COLD EARLY HISTORY? P. B. Niles¹ and J. Michalski^{2,3},
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Introduction: The martian climate has long been thought to have evolved substantially through history from a warm and wet period to the current cold and dry conditions on the martian surface [1]. This view has been challenged based primarily on evidence that the early Sun had a substantially reduced luminosity and that a greenhouse atmosphere would be difficult to sustain on Mars for long periods of time [2]. In addition, the evidence for a warm, wet period of martian history is far from conclusive with many of the salient features capable of being explained by an early cold climate [3, 4]. An important test of the warm, wet early Mars hypothesis is the abundance of carbonates in the crust [1].

Recent high precision isotopic measurements of the martian atmosphere and discoveries of carbonates on the martian surface provide new constraints on the evolution of the martian atmosphere [5-8]. This work seeks to apply these constraints to test the feasibility of the cold early scenario.

Methods: A stepwise CO₂ evolution model was constructed that calculates the CO₂ pressure in the martian atmosphere from 3.9 Ga to the present. Atmosphere thickness present at 3.9 Ga (used as the starting condition) was varied in the model runs and assumed to have $\delta^{13}\text{C}$ of +26‰ in equilibrium with the average ALH 84001 carbonate [9]. Magmatic degassing was based on estimates of crustal production [10, 11]. Estimates of atmospheric loss of CO₂ on Mars range from as few as 45 mbars [12] to as much as 3 bars [13]. Our estimates are scaled to ~300 mbars following calculations described in [14]. Carbonate precipitation is assumed to occur evenly through time at a rate proportional to the atmospheric density.

Results: The constraints provided by the isotopic measurements are met using assumptions consistent with a cold early Mars. Carbonate precipitation is the most significant sink of CO₂ which both reduces the overall amount of atmospheric CO₂ as well as balancing the substantial fractionation caused by atmospheric loss (Fig. 1). Volcanic degassing occurring since 3.9 Ga is only a minor portion of the overall CO₂ budget and has a negligible effect on the modeling. Assuming a 1 bar atmosphere at 3.9 Ga, the model predicts that 840 mbars of CO₂ would be stored as carbonate which amounts to 1.6% of the upper 1 km of Mars. This would be in addition to any carbonates formed prior to 3.9 Ga.

The model predicts an average carbonate $\delta^{13}\text{C}$ of +69‰ which is higher than any carbonate found in the martian meteorites. If a large enough fraction of the early atmosphere was lost via sputtering and photochemical processes since 3.9 Ga then we should expect the average $\delta^{13}\text{C}$ of carbonates to be very high (>~50‰) to balance the amount of ¹²C lost to space and maintain a low modern atmospheric value. Thus, if the model utilized a reduced atmospheric loss calculation similar to [12], the average $\delta^{13}\text{C}$ of the carbonate on Mars would be reduced to near +35‰.

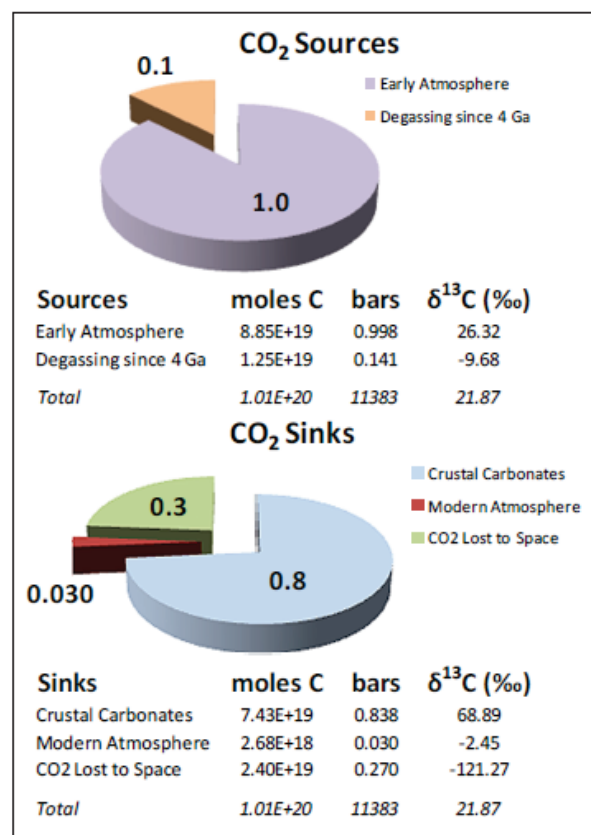


Figure 1. Model output for 1 bar atmosphere at 3.9 Ga.

Discussion: This work assumes that the bulk of the processes of primordial degassing, hydrodynamic escape, and impact erosion all occurred prior to 3.9 Ga and are accounted for in the starting conditions. Presumably the average $\delta^{13}\text{C}$ value of the ALH 84001 carbonates (~+40‰ [9]) is broadly representative of the atmosphere at that time enriched through atmospheric loss.

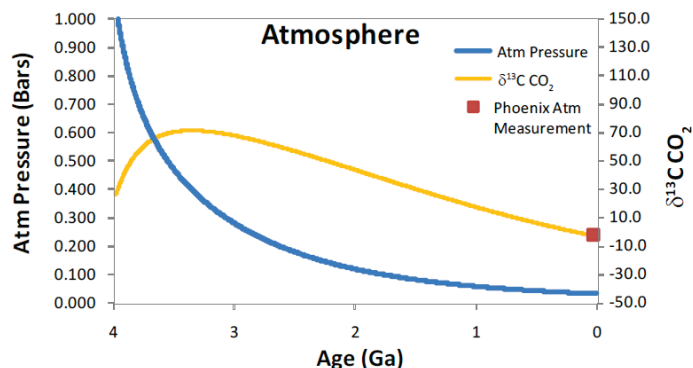


Figure 2. Displays the evolution of CO₂ pressure and isotopic composition from 3.9 Ga to the present in the stepwise model.

Our modeling shows that an early cold martian climate is consistent with the constraints set by the abundance and isotopic composition of CO₂ and carbonates on Mars (Fig. 2). This self-consistent history of CO₂ evolution contains no “missing” carbonates and a 1 bar of CO₂ is not seen as being sufficient to warm the planet even in the presence of substantial SO₂ [15].

Martian dust contains 2-5% carbonate [16] and may be a representative sample of the upper crust of Mars. If the upper 1 kilometer of crust of Mars contains only 4% carbonate, then it can account for 2 bars of CO₂. Assuming that 1 bar of CO₂ was sequestered into the crust prior to 3.9 Ga, and additional CO₂ was lost to early hydrodynamic escape and impact events, it is reasonable to think that the atmosphere at 3.9 Ga was about 1 bar as assumed in this study. If atmospheric pressures were substantially more than 1 bar at 3.9 Ga then much more extensive buried carbonate reservoirs similar to the recently discovered deep crustal carbonates [8] remain to be found.

Oxygen isotopes reveal an important discrepancy that may inform climactic conditions and history on Mars as well. All of the weathering products and water measured thus far from the martian meteorites spanning a range of 4 billion years have shown a $\Delta^{17}\text{O}$ anomaly indicating that they formed from a reservoir of oxygen that is not in equilibrium with the lithosphere of the planet [17, 18]. However, oxygen isotopes in atmospheric CO₂ indicate that the oxygen reservoir has been buffered through exchange with the lithosphere over time preventing an enrichment of ^{18}O by atmospheric loss [5]. This suggests that predominant weathering styles on Mars may be very different from the Earth and what might be expected from a warm, wet early history [19].

This discrepancy can be resolved if the weathering on Mars occurred in a cold climate. We suggest a model where weathering occurs in a top-down manner driven by precipitation of snow, dust, and acidic aero-

sols [20]. This is in contrast to a bottom-up model driven by groundwater upwelling in a warmer climate in the late Noachian and early Hesperian [21]. In this cold ice-weathering model, the majority of the weathering on Mars occurred as dust interacted with thin films of water stabilized by acidic aerosols. These dust-ice mixtures were collected in large layered deposits at low latitudes during high obliquity or polar wander events. Basal melting of these deposits resulted in groundwater sapping and fluvial channel formation [4]. Sublimation of these deposits left behind a residue of hydrated aggregates that were subsequently reworked by eolian processes [20].

The atmospheric dominance in these systems would allow simultaneous exchange of ^{18}O and ^{17}O between silicate dust particles, water and ^{17}O rich ozone, preserving an $\Delta^{17}\text{O}$ anomaly in the secondary minerals.

A denser atmosphere may have been possible during the early Noachian (prior to 3.9 Ga) and it is extremely likely that warm enough conditions existed for at least brief periods due to large volcanic eruptions or impact events [22] through the late Noachian and Hesperian. As the planet cooled and heat flows decreased at the end of the Noachian, less frequent melting events were possible [4].

References: 1. Pollack, J.B., et al., *Icarus* **71**, 203-224 (1987). 2. Kasting, J.F., *Icarus* **94**, 1-13 (1991). 3. Gaidos, E. and G. Marion, *J. Geophys. Res.-Planets* **108** (2003). 4. Carr, M.H. and J.W. Head, *Geophys. Res. Lett.* **30** (2003). 5. Niles, P.B., et al., *Science* **329**, 1334-1337 (2010). 6. Ehlmann, B.L., et al., *Science* **322**, 1828-1832 (2008). 7. Morris, R.V., et al., *Science* **329**, 421-424 (2010). 8. Michalski, J.R. and P.B. Niles, *Nat. Geosci.* **3**, 751-755 (2010). 9. Romanek, C.S., et al., *Nature* **372**, 655-657 (1994). 10. Hirschmann, M.M. and A.C. Withers, *Earth Planet. Sci. Lett.* **270**, 147-155 (2008). 11. Greeley, R. and B.D. Schneid, *Science* **254**, 996-998 (1991). 12. Johnson, R.E., D. Schnellenberger, and M.C. Wong, *J. Geophys. Res.* **105**, 1659-1670 (2000). 13. Kass, D.M. and Y.L. Yung, *Science* **268**, 697-699 (1995). 14. Manning, C.V., C.P. McKay, and K.J. Zahnle, *Icarus* **180**, 38-59 (2006). 15. Tian, F., et al., *Earth Planet. Sci. Lett.* **295**, 412-418 (2010). 16. Bandfield, J.L., T.D. Glotch, and P.R. Christensen, *Science* **301**, 1084-1087 (2003). 17. Farquhar, J. and M.H. Thiemens, *J. Geophys. Res.-Planets* **105**, 11991-11997 (2000). 18. Farquhar, J., M.H. Thiemens, and T. Jackson, *Science* **280**, 1580-1582 (1998). 19. Eiler, J., Sagan Lecture at the American Geophysical Union, San Francisco 2010. 20. Niles, P.B. and J. Michalski, *Nat. Geosci.* **2**, 215-220 (2009). 21. Andrews-Hanna, J.C., R.J. Phillips, and M.T. Zuber, *Nature* **446**, 163-166 (2007). 22. Segura, T.L., et al., *Science* **298**, 1977-1980 (2002).